Percolation and Polymer-based Nanocomposites

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Outline

- Fiber-based composites & percolation: the “What” and the “Why”

- Elastic moduli in rod-reinforced nanocomposites:
  Integrating percolation ideas with effective medium theory

- Analogy between continuum rod percolation and site percolation on a modified Bethe lattice: percolation thresholds for polydisperse rods

- A model for systems with non-random spatial distributions for the fibers: Effects due to particle clustering and correlation: Implications of “quality of dispersion” for electrical conductivity

- Percolation and conductivity in polydisperse systems of aligned rods, the impact of rod alignment upon conductivity, and some results for polydisperse circular disks

- Pore size distribution and tracer diffusion in fiber networks

- Future Directions and Acknowledgements
Composites & Percolation

**Composites**: Mixtures of particles/nanoparticles (the “filler”), dispersed (randomly or otherwise) within another phase (the “matrix”)

Basic idea: to combine & integrate desirable properties (e.g., low density, high mechanical moduli or conductivity) from different classes of material

Natural Composites (e.g. bone and wood) often exhibit hierarchical structures, varying organizational motifs on different scales

“Wood for the Trees”: wood remains one of the most successful fiber-reinforced composites, and cellulose the most widely-occurring biopolymer (annual global production of wood ~ $1.75 \times 10^9$ metric tons)
Wood: A natural, fiber-reinforced composite

Cell walls: layered cellulose microfibrils (linear chains of glucose residues, degree of polymerization ~ 5000 – 10000, ~ 40-50 % w/w of dry wood depending on species), bound to matrix of hemicellulose and lignin.

Cellulose Nanocrystals (I)

Cellulose (linear chains of glucose residues), bound to matrix of lignin and hemicellulose, comprises ~ 40-50 % w/w of dry wood

Individual fibers have major dimensions ~ 1-3 mm, consisting of spirally wound layers of microfibrils bound to lignin-hemicellulose matrix; microfibrils contain crystalline domains of parallel cellulose chains; individual crystalline domains ~ 5-20 nm in diameter, ~ 1-2 μm in length

Nanocrystalline domains separable from amorphous regions by controlled acid hydrolysis (amorphous regions degrade more rapidly)

Crystalline domain elastic modulus (longitudinal) ~ 150 GPa: compare martensitic steel ~ 200 GPa, carbon nanotubes ~ 10^3 GPa

*Suggests possible role for cellulose nanocrystals as a renewable, bio-based, low-density, reinforcing filler for polymer-based nanocomposites*
Cellulose Nanocrystals (II)

- Cellulose microfibrils secreted by certain non-photosynthetic bacteria (*e.g.* *Acetobacter xylinum*), and form the mantle of sea-squirts (“tunicates”) (*e.g.* *Ciona intestinalis*).

- These highly pure forms are free from lignin/hemicelluloses; fermentation of glucose a possible microbial route to large-scale cellulose production.

**Connectedness Percolation: What?**

**Percolation:** The formation of infinite, spanning clusters of “connected” (defined by spatial proximity) particles.

\[ \phi < \phi^* \]: Below percolation threshold

\[ \phi > \phi^* \]: Above percolation threshold
Percolation: Why? Dramatic Effects on Material Properties

Impact Toughness:

$\tau$ – Matrix ligament thickness

Toughness of HDPE/Rubber Composites
Rubber particle size range: 0.36 ~ 0.87 mm
Electrical conductivity and Elastic Modulus (I)

- Polypyrrole-coated cellulose whiskers investigated as electrically conducting filler particles: (L. Flandin, et al., Compos. Sci. Technol., 61, 895, (2001); Mean aspect ratio ~ 15)

- Mechanical reinforcement/modulus enhancement: (tunicate cellulose whiskers in poly-(S-co-BuA), V. Favier et al., Macromolecules, 28, 6365, (1995); Mean aspect ratio ~ 70)
Polystyrene (PS) reinforced with Multi-Walled Carbon Nanotubes (MWCNTs): (Diameters: 150 – 200 nm; Lengths: 5 – 10 μm; T = 190° C; critical volume fraction ≈ 0.019; A.K. Kota, et al., Macromolecules, 40, 7400, (2007))
Percolation Thresholds for Rod-like Particles

Percolation threshold for rods, $\phi^* \sim (D/L)$, depends approximately inversely upon aspect ratio, a result supported by:


Elasticity: Stress, Strain, & Stiffness

- Stress tensor: \{\sigma\} (Energy/Volume)
- Strain tensor: \{\varepsilon\} (Dimensionless)
- Stiffness tensor: \{C\} (Energy/Volume): Fourth rank tensor
- \{C\} can have a maximum of 21 independent elements/elastic coefficients
- For an isotropic system, there are only TWO independent elastic constants, usually chosen from amongst: \{E, G, K, \nu\} (tensile, shear, and bulk modulus, and Poisson ratio, respectively)
- In terms of deformation energy per unit volume, \(U\):
  \[
  E = \frac{u^{(2)}_{yz} \left( 3u^{(2)}_{zz} - u^{(2)}_{yy} \right)}{\left( 4u^{(2)}_{zz} - u^{(2)}_{yz} \right)} \quad \text{and:} \quad G = \frac{u^{(2)}_{yz}}{4}
  \]
  \[
  u^{(2)}_{nm} = \left. \frac{\partial^2 U}{\partial \varepsilon_{nm}^2} \right|_{\varepsilon \to 0}
  \]
A Seismic Interlude

Seismic (earthquake-generated) waves:

- Primary/Pressure ("P-waves"): Longitudinal
  \[ V_p = \sqrt{\left( K + \frac{4G}{3} \right) / \rho} \]
  \( \approx 5\text{-}7 \text{ km/s in crust, } \approx 8 \text{ km/s in mantle} \)

- Secondary/Shear ("S-waves"): Transverse
  \[ V_s = \sqrt{G / \rho} \]
  \( \approx 3\text{-}4 \text{ km/s in crust, } \approx 5 \text{ km/s in mantle} \)
  Cannot traverse liquid outer core of the earth

"Shadow zones" and travel times reveal information regarding internal structure of the earth

(Courtesy US Geological Survey)
Elastic Moduli of Composite Materials

Simple estimates employing only: (i) the volume fractions \( \{ \phi_n \} \), and: (ii) the elastic coefficients \( \{ E_n \} \), of the individual constituents, include the Voigt-Reuss and Hashin-Shtrikman bounds (for isotropic materials) (Z. Hashin and S. Shtrikman, *J. Mech. Phys. Solids*, 11, 127, (1963))

\[
E_V^* = \phi_1 E_1 + \phi_2 E_2 \quad \frac{1}{E_R^*} = \frac{\phi_1}{E_1} + \frac{\phi_2}{E_2}
\]


Voigt / “Parallel”    Reuss / “Series”
Percolation and Elastic Moduli

Cellulose nanocrystals modeled as circular cylinders, uniform radius \( R \), variable lengths \( L \).

Nanocrystals modeled as being transversely isotropic, with five independent elastic constants: \( \{E_{ax}, E_{tr}, G_{tr}, \nu_{ax}, \nu_{tr}\} \).

\[ E_{ax} = 130 \text{ GPa},\ E_{tr} = 15 \text{ GPa},\ G_{tr} = 5 \text{ GPa},\ \nu_{ax} = \nu_{tr} = 0.3 \]


Objective: To unify percolation ideas with effective medium theory towards an integrated model for composite properties.
Model for Network Contribution to Elasticity

For network element of length \( L \) and radius \( R \): elastic deformation energy \( U \) is:

\[
U = \frac{\pi E_{ax} R^2 L \varepsilon_{zz}^2}{2} + \frac{3\pi R^2 L E_{ax} \left( \varepsilon_{xz}^2 + \varepsilon_{yz}^2 \right)}{\left( 8L^2/R^2 + 9E_{ax}/G_{tr} \right)}
\]

Combines stretching, bending, shearing energies, \( \{\varepsilon_{ij}\} \) are strain components in fiber-fixed frame, with fiber axis in the Z-direction (F. Pampaloni, et al., Proc. Natl. Acad. Sci. US., 103, 10248, (2006))

Assume: (i) isotropic orientational distribution, (ii) random contacts between rods, Poisson distribution for lengths of network elements, and (iii) affine deformation

Energy of elastic deformation averaged over rod and segment lengths and orientations, strain tensor transformed to laboratory frame, then differentiated twice with respect to \( \{\varepsilon_{ij}\} \) to obtain estimates for the network moduli \( \{E_{net}, G_{net}\} \)

\textbf{BUT}: Rods of different lengths will differ in likelihood of belonging to network, and for small enough volume fractions, no network exists!
Percolation Probability and Threshold

Percolation probability, denoted \( P(\phi, L) = \) probability that a randomly selected rod of length \( L \) belongs to the percolating network/infinite cluster.

Modeled as: \( P(\phi, L) = 1 - e^{-\alpha(\phi - \phi^*(L))} \) for \( \phi > \phi^*(L) \), and zero otherwise.

\[ \phi^*(L) \approx n_c^*(R/L), \text{ } L\text{-dependent percolation threshold} \]

Parameters \( \{ \alpha, n_c^* \} \) are treated as adjustable: control transition width & location of threshold.

These assumptions, together with piecewise-linear (unimodal) model for the overall distribution over rod lengths \( L \), allows estimation of:
(i) volume fraction of rods belonging to network \( (\phi_{net}) \),
(ii) volume fraction and length distribution of rods that remain dispersed,
(iii) average length of network elements (assuming random contacts).

There remains the task of combining the network moduli with contributions from the matrix, and from the dispersed rods.
Moduli for the Composite

Identify a “continuum surrogate” for network, using “Swiss cheese” analogy, where:
(matrix + dispersed rods) → (spherical voids)

Use Mori-Tanaka (MT) model to estimate moduli for an isotropic system made up of:
(matrix + dispersed rods) (Dispersed rods treated as length-polydisperse, within a discrete

Final step: again use Mori-Tanaka (MT) method to estimate moduli for the system:
(continuum network surrogate) + (spherical voids now filled with isotropic system of
{matrix + dispersed rods}, with moduli determined in previous step)

Recursive use of MT model: equivalent in this context to Hashin-Shtrikman upper
bound
Results (I)

- Matrix: Copolymer of ethylene oxide + epichlorohydrin (EO-EPI)
- Filler: Tunicate cellulose whiskers (solution cast system)
- Mean whisker radius $R = 13.35$ nm
- Whisker Lengths: $L_n = 2.23$ $\mu$ m, $L_{\text{max}} = 5.37$ $\mu$ m (reproduces first two moments of experimentally measured distribution)
- Solid Line: Polydispersity in rod lengths included in model
- Broken Line: Model treats rods as monodisperse, $f(L) = \delta(L - L_n)$

$\log\left(\frac{E^*}{E_{\text{matrix}}}\right)$

Results (II)

- Matrix: waterborne polyurethane (WPU)
- Filler: Flax cellulose nanocrystals
- Mean whisker radius $R = 10.5$ nm
- Whisker Lengths: $L_n = 327$ nm, $L_{max} = 500$ nm (based on experimentally measured distribution of rod lengths)
- Solid Line: Polydispersity in rod lengths included in model
- Broken Line: Model treats rods as monodisperse, $f(L) = \delta(L - L_n)$

Results (III)

- Matrix: Copolymer of styrene + butyl acrylate (poly-(S-co-BuA))
- Filler: Tunicate cellulose whiskers
- Mean whisker radius $R = 7.5$ nm
- Whisker Lengths: $L_n = 1.17 \, \mu\text{m}$, $L_{\text{max}} = 3.0 \, \mu\text{m}$ (based on experimentally measured distribution of rod lengths)
- Solid Line: Polydispersity in rod lengths included in model
- Broken Line: Model treats rods as monodisperse, $f(L) = \delta(L - L_n)$

Can Continuum Rod Percolation be related to Percolation on the Bethe Lattice?

- Perfect dendrimer/Cayley tree, with uniform degree of branching = \( z \) at each vertex
- No loops/closed paths available
- Extensively studied as exemplar of mean-field lattice percolation
- If vertices are occupied with probability \( \xi \), then site percolation threshold located at: \( \xi^* = (1/(z - 1)) \)
- Given how thoroughly this problem has been examined, question arises whether one can relate continuum rod percolation to percolation on the Bethe lattice

Portion of a Bethe lattice with \( z = 3 \)
Continuum Rod Percolation ↔ Bethe Lattice: A simple-minded mapping:

Consider a population of rods, with uniform radius = $R$, but variable lengths $L$. We let $f(L)$ denote the distribution over rod lengths.

On average: a rod of length $L$ experiences $\sim \phi (L/R)$ contacts with other rods in the system.

For a Bethe lattice with degree $z$: each occupied site has (on average) $z \xi$ "contacts" with nearest neighbor occupied sites.

Suggests the following analogy:

- Rod ↔ Occupied lattice site
- $\phi \leftrightarrow \xi$
- $z \leftrightarrow z(L) \leftrightarrow (L/R)$

The corresponding Bethe lattice must have a distribution of vertex degrees.
Percolation on a modified Bethe Lattice:

Bethe Lattice Analog: Site percolation on a modified Bethe lattice, with site occupation probability $= \phi$, and with vertex degree distribution $f(z)$ that can be obtained from the underlying rod length distribution.

Let $Q$ = Probability that a randomly chosen branch in such a lattice, for which it is known that one of the terminal sites is occupied, does not lead to the infinite cluster.


$$Q(\phi) = 1 - \phi + \phi \sum_z \left( \frac{z f(z)}{\langle z \rangle} \right) Q^{(z-1)}$$

where the summation runs over all values of $z (L)$, and $Q$ depends only upon $\phi$ and $f(z)$. 

Illustration of a portion of modified Bethe lattice.
Percolation Threshold and Probability:

- Percolation probability for a rod of length $L = \text{probability that an occupied site with vertex degree } z(L) \text{ belongs to the infinite cluster}

\[ P(\phi,L) = 1 - \{Q(\phi)\}^{z(L)} \]

- Percolation threshold = value of $\phi$ at which a solution exists for $Q$ other than the trivial solution $\{Q = 1, P = 0\}$:

\[ \phi^* = \frac{\langle z(L) \rangle}{(\langle z^2(L) \rangle - \langle z(L) \rangle)} \approx \frac{\langle R(L) \rangle}{\langle L^2 \rangle} \approx \frac{R}{L_w} \]

for the case that $L >> R$ for all rods in the system (A.P. Chatterjee, J. Chem. Phys., 132, 224905, (2010); an identical result was derived in the field of “scale free” (power law) networks some years ago: R. Albert and A.-L. Barabasi, Rev. Mod. Phys., 74, 47, (2002))

Generalization to finite-diameter rods:

Model rods as hard core + soft shell entities: hard core radii and lengths denoted: \( \{R, L\} \), and soft shell radii and lengths given by: \( \{R + \lambda, L + 2 \lambda\} \)

For this problem, an identical approach yields: (A.P. Chatterjee, J. Stat. Phys., 146, 244, (2012)):

\[
\phi_c \approx \frac{\langle R^2 L \rangle}{\lambda \langle L^2 \rangle}
\]


Result can be generalized to particles with arbitrary cross-sectional shapes, not just circular cylinders (A.P. Chatterjee, J. Chem. Phys., 137, 134903, (2012))
Network and Backbone Volume Fractions:

A particle is said to belong to the “backbone” of the network if it experiences \textit{at least two} contacts with the infinite cluster.

Let \( B(z(L)) = \) Probability that a rod of length \( L \) belongs to the backbone.

Then: 
\[
B(z) = z\left(1 - \left(1 - P(z)^{(z-1)/z}\right)\right) - (z-1)P(z) \quad (R.G. Larson and H.T. Davis, J. Phys. C, 15, 2327, (1982))
\]

Volume fractions occupied by the network, and network backbone:

\[
\phi_{net} = \left(\phi / L_n\right) \int_0^\infty dLLf(L)P(z(L)), \quad \phi_{bb} = \left(\phi / L_n\right) \int_0^\infty dLLf(L)B(z(L))
\]

Near Threshold:

\[
\phi_{net} \approx 2\left(L_w / L_z\right)(\phi - \phi^*), \quad \phi_{bb} \approx 2\left(L_w / R\right)\left(L_w / L_z\right)(\phi - \phi^*)^2
\]

where \( L_w, L_z \) are weight and \( z \)-averaged rod lengths, respectively.

Percolation & Backbone Probabilities:

- Polydisperse Rods: Unimodal Beta distribution, with: \( L_{\text{min}} = 8.33 \ R, \ L_{\text{max}} = 800 \ R, \ L_n = 66.67 \ R, \ L_w = 100 \ R = 1.5 \ L_n, \ L_z = 133.34 \ R = 2 \ L_n \):
  → **Black curves**

- Monodisperse Rods (for comparison): \( L_n = L_w = L_z = 100 \ R \), same percolation threshold as the polydisperse rod population:
  → **Red curves**

![Graph](graph.png)

Upper Black Curves: \( L = L_{\text{max}} \)
Lower Black Curves: \( L = L_{\text{min}} \)

Solid: \( P(\phi, L) \)
Broken: \( B(\phi, L) \)
Network & Backbone Volume Fractions:

- **Polydisperse Rods**: Unimodal Beta distribution, with: $L_{\text{min}} = 8.33 \, R$, $L_{\text{max}} = 800 \, R$, $L_n = 66.67 \, R$, $L_w = 100 \, R = 1.5 \, L_n$, $L_z = 133.34 \, R = 2 \, L_n$:
  → **Black curves**

- **Monodisperse Rods** (for comparison): $L_n = L_w = L_z = 100 \, R$, same percolation threshold as the polydisperse rod population:
  → **Red curves**

Network, backbone, volume fractions *lower* for polydisperse system
Comparison with Monte Carlo Simulations (I):


- MC results show reasonable agreement with theory

\[ p = \text{Number fraction of long rods for bidisperse systems} \]

Symbols = MC results, various values of \( p \) and distributions of aspect ratios

Solid Line = Theory based upon modified Bethe lattice
Comparison with Monte Carlo Simulations (II): Monodisperse Spherocylinders:

- MC results show reasonable agreement with theory (A.P. Chatterjee, J. Phys.: Condensed Matter, 27, 375302, (2015))

Symbols = MC results

Solid Line = Theory based upon Bethe lattice approach

$L = $ Spherocylinder length; $\eta_c = $ Volume fraction occupied by (hard cores + soft shells)

$\lambda = $ Diameter of (hard core + soft shell)

$D = $ Hard core diameter; $\lambda = 1.2 \, D$
Average number of Contacts at Threshold:

- Average number of contacts per particle at threshold:
  \[ N_c = \frac{\langle z \rangle^2}{\langle z^2 \rangle - \langle z \rangle} \]
  where \( z \) is the vertex degree in the modified Bethe lattice

- For polydisperse systems, \( N_c \) can be smaller than unity


\[ p = \text{Number fraction of long rods, bidisperse systems} \]
Symbols = MC results, various aspect ratio distributions

A similar result (\( N_c < 1 \)) has been reported for hyperspheres in high-dimensional spaces (N. Wagner, I. Balberg, and D. Klein, Phys. Rev. E, 74, 011127, (2006))
Non-random Spatial Distribution of Particles: Clustering and Correlation Effects:

Foregoing results assume particles are distributed in a spatially random, homogeneous fashion.

But: particle distribution may in reality display local clustering or aggregation, particle contact numbers may be altered by correlation effects: “Quality of dispersion” can be variable.

VERY SIMPLE & STRICTLY OPERATIONAL microstructural descriptors that capture such mesoscale non-randomness:

(i) Clustering parameter, $p$: Measures degree of clustering

(ii) Correlation parameter, $K$: Measures degree of rod-rod correlation, using the Quasi-Chemical Approximation (“QCA”)

Model separates effects upon percolation due to (i) polydispersity, (ii) clustering, and (iii) particle correlation.
Parameters quantifying degrees of Clustering and Correlation:

**CLUSTERING:** $p = \text{Number fraction of sites with a given vertex degree } z \text{ that enjoy fully tree-like local environments; the remainder belong to fully connected subgraphs}.$

$p$ relates inversely to “Clustering coefficient”, $C$, where $C = \text{Probability that a pair of rods } X \text{ and } Y, \text{ each of which touches a given (other) rod } Z, \text{ also touch each other } (D.J. \text{ Watts and S.H. Strogatz, Nature, 393, 440, (1998)})$.

**CORRELATION:** $K = p_{10}^2/p_{00}p_{11}$, where: $p_{ij} = \text{probability that any randomly selected pair of directly connected sites have the occupancy states } i \text{ and } j$.

$p = 1 \iff \text{Fully unclustered, and } p = 0 \iff \text{Maximally clustered}$

Increase in $K \iff \text{Fewer rod-rod contacts for fixed rod volume fraction, rods more likely to be entirely enveloped by matrix}$.
Modified Bethe Lattice to address Particle Clustering Effects:

- Modified lattice includes fraction of fully connected subgraphs to model particle clustering ($p$)

- Correlation between occupation states of neighboring sites described within QCA ($K$)

- Percolation threshold can be expressed as function of:
  (i) polydispersity, (ii) degree of clustering, and (iii) strength of rod-rod correlations. Volume fractions occupied by network and network backbone, and percolation probabilities, can also be estimated

Effects of Particle Clustering on Conductivity in Nanotube Networks:


- For given (i) volume fraction, (ii) polydispersity, and degrees of (iii) clustering and (iv) correlation, determine the soft shell thickness for which particles just form a percolating cluster/network

\[ \sigma(\phi) = \sigma_0 e^{-4\lambda(\phi)/\xi} \]

- \( \lambda = \) soft shell thickness, and:
  - \( \xi = \) electron tunneling range

- Predicts *monotonic but non-power-law* increase in the conductivity with particle volume fraction
Model Predictions:

- Limiting results for very small rod volume fractions:

- When $p = 1$, fully unclustered:
  \[
  \frac{\sigma(\phi)}{\sigma_0} \approx e^{-4KR^2/\xi L_w \phi}
  \]

  and:

- When $p = 0$, maximally clustered:
  \[
  \frac{\sigma(\phi)}{\sigma_0} \approx e^{-4K^2R^2/\xi L_n \phi^2}
  \]

Conductivity in a CNT-based composite:


- $L = 5.5 \, \mu m$, $R = 6.25 \, nm$, modeled as monodisperse; $\xi = 1 \, nm$, $p = 0$ (maximal clustering) and $K = 1.3$; Conductivity in units of S/m

Conductivity: Correlation effects:

- $L = 516 \text{ nm}$, $R = 0.675 \text{ nm}$, modeled as monodisperse; $\xi = 1 \text{ nm}$; Conductivity in S/cm

- Triangles: Sonicated during curing
- Diamonds: NOT sonicated during curing

Solid Lines:
- $p = 1$ (fully tree-like, unclustered, both cases): $K = 0.32$ (upper) & $K = 1.1$ (lower)

Broken Lines:
- Thresholds: 0.000052 (upper), and 0.0001 (lower)
- Exponents: 2.7 (upper), and 1.6 (lower)
Percolation in Aligned/Oriented Rods:

- Shear flow, or external fields, can induce orientational/nematic order and alignment among rod-like particles.

- Degree of order described by orientational order parameter, denoted: $< S > = < P_2 (\cos(\theta)) >$

- Excluded volume depends upon aspect ratio as well as order parameter.

Isotropic  $\rightarrow$  Nematic
Percolation in Aligned/Oriented Rods: Monodisperse Case:

Analogy to lattice percolation problem can be generalized to treat oriented/aligned polydisperse rods.

For monodisperse rods: Alignment/orientational ordering raises the percolation threshold.

Percolation threshold for rods with aspect ratios (\(L/R\)) equal to 20 (upper) and 100 (lower) as functions of the order parameter.

Connectedness range, \(\lambda = 0.1 R\)

Percolation in Aligned/Oriented Rods: Polydisperse (Bidisperse) Case:

For polydisperse systems: Degree of alignment may depend upon aspect ratio, leading to some interesting effects:

Percolation threshold for bidisperse rods with aspect ratios ($L/R$) equal to 20 and 100 as functions of the number fraction of short rods

Connectedness range, $\lambda = 0.1\ R$

Short Rods: Isotropic
Long Rods: from top to bottom: Order parameter equals: 0.99, 0.9, 0.5, and zero (isotropic, dotted line)

Isotropic short rods can act as “linkers” between oriented long rods

Conductivity, Percolation, and Degree of Alignment:

Critical Path Approximation (“CPA”) is combined with:

(ii) a flexible approximation for the rod orientational distribution function, and:
(iii) percolation model, to estimate the conductance in composites as functions of both the volume fraction and the degree of particle alignment

Basic findings:

(i) Increasing degree of alignment lowers conductivity, and:
(ii) Conductivity depends strongly upon not only mean orientational order parameter ($<S>$), but also upon the standard deviation in the order parameter: fluctuations in the orientational order parameter can have significant effect (A.P. Chatterjee and C. Grimaldi, *J. Phys.: Condensed Matter*, 27, 145302, (2015))
Competing Effects:

As degree of alignment increases:
(i) distance of nearest approach of rod surfaces increases, reducing conductivity, but also:
(ii) rod-to-rod tunneling conductance is higher the more close to parallel the rods axes are, for a given separation between the rods

Experiment on SWCNT/PMMA composite (S.I. White, et al., Phys. Rev. B, 79, 024301, (2009)) reports that conductivity does indeed decrease with rise in the degree of alignment, but the trend may not be monotonic (SWCNT aspect ratio, $L/R = 90$)

An unorthodox choice for the Orientational Distribution Function ("ODF"):

- We describe the distribution over rod orientations using the function:

\[ f(\theta) = a + b |\cos(\theta)|^m \]

where both \( b \) and \( m \) are required to be positive.

- For this choice of ODF:

\[
\langle S \rangle = \langle P_2(\cos(\theta)) \rangle = \frac{4\pi bm}{(m+1)(m+3)}
\]

and:

\[
\langle S^2 \rangle = \langle \{P_2(\cos(\theta))\}^2 \rangle = \frac{1}{5} \left[ 1 + \frac{2(2m+1)\langle S \rangle}{(m+5)} \right]
\]

- Mean value and standard deviation in the orientational order parameter can be varied independently

- For a fixed value of \( \langle S \rangle \), the standard deviation of \( S \) increases monotonically with increasing values of \( m \)
Conductivity and Particle Alignment (I):

- Our choice for orientational distribution function ("ODF") permits independent variation of the mean value and standard deviation of the order parameter $S$.

- Conductivity is calculated from (i) the \{CPA + percolation\} approach, and (ii) using an effective medium approximation ("EMA") (B. Nigro and C. Grimaldi, *Phys. Rev. B*, **90**, 094202, (2014)).

- EMA & \{CPA + Percolation\} approaches agree closely, both find conductance sensitive to standard deviation of $S$.

Rods with $L = 200 \, R$; Tunneling decay length, $\xi = 0.2 \, R$; $p = K = 1$ in percolation model; $\phi = 0.01$, all cases.

SOLID LINES: Percolation approach

BROKEN LINES: EMA approach

UPPER: Minimum standard deviation in $S$ our model allows for given $< S >$

LOWER: Maximum standard deviation in $S$ our model allows for given $< S >$

Conductivity and Particle Alignment (II):


- Soft shell thickness required in the {CPA + Percolation} approach reflects the orientational distribution function

- Clustering, particle correlation effects can be modeled via parameters \{p, K\}

Rods with \(L = 200\ R\); Tunneling decay length, \(\xi = 0.2\ R\); \(p = K = 1\) in percolation model

UPPER DOTTED LINE: Isotropic system, EMA
LOWER DOTTED LINE: Isotropic system, CPA

SOLID LINES: Percolation approach, \(< S > = 0.8\)
DASHED LINES: EMA approach, \(< S > = 0.8\)

FOR SOLID AND DASHED LINES:
UPPER: Minimum standard deviation in \(S\) our model allows for given \(< S >\)
LOWER: Maximum standard deviation in \(S\) our model allows for given \(< S >\)
**Inter-Penetrable Spheres and Disks:**

**More complex:** Here, we use the accurate Carnahan-Starling approximation for the contact value of the radial distribution function in order to estimate the numbers of contacts, and to establish the mapping onto a lattice problem:

\[ g_{CS}^{3D}(\sigma) = \frac{(1 - \eta/2)}{(1 - \eta)^3}, \quad \eta = \frac{4\pi \rho R^3}{3} \]

\[ g_{CS}^{2D}(\sigma) = \frac{(1 - \alpha \eta)}{(1 - \eta)^2}, \quad \alpha = \frac{2\sqrt{3}}{\pi} - \frac{2}{3}, \quad \eta = \pi \rho R^2 \]

Application to Penetrable Spheres (3D):

- \( R \) = hard core radius, and 
  \( \lambda \) = soft shell/connectedness range

- Symbols: MC simulations 

- Broken line: Theory with:
  \[ \rho = 0.017 + 0.12\left[\frac{R}{(R + \lambda)}\right]^3 \]

Corresponds to a monotonic decrease in the degree of clustering with diminishing soft shell thickness/connectedness range, for a fixed hard core radius
Application to Penetrable Disks (2D):

- $R =$ hard core radius, and
  $\lambda =$ soft shell/connectedness range


- Broken line: Theory with:

$$p = 0.02\left[\frac{R}{(R + \lambda)}\right]^{1.5}$$

**Note:** In this case, a constant of proportionality has been used to relate the disk volume fraction to site occupation probability such that agreement with the simulation is enforced as $R \to 0$, for $p = 0$

Corresponds to a monotonic decrease in the degree of clustering with diminishing soft shell thickness/connectedness range, for a fixed hard core radius.
Application to Penetrable Rectangles (2D):

- Monodisperse, randomly oriented, penetrable rectangles in 2D

- Predictions from theory (treating the system as entirely unclustered, $\rho = 1$) are in good semi-quantitative agreement with MC simulations

Vertical Axis: Normalized percolation threshold

Horizontal axis: Reciprocal of aspect ratio


Polydisperse Circular Disks in 3D:


- Consider the limiting cases of (i) perfectly random, isotropic, disk orientations, and (ii) perfectly aligned, fully nematic, arrangements
Circular Disks in 3D: Monodisperse Case

- For both isotropic and perfectly aligned monodisperse disk systems: for a fixed value of \((\lambda / L)\) where: \(L = \) disk thickness, \(R = \) disk radius, and \(\lambda = \) connectedness range: as \((R / L)\) increases, the threshold increases monotonically towards a plateau (A.P. Chatterjee, *J. Chem. Phys.*, 141, 034903, (2014))

- Qualitatively consistent with MC results, except for small aspect ratios

- Threshold always larger for nematic than for isotropic distributions

Solid – Isotropic
Dashed – Fully aligned, nematic
Upper: \(\lambda = 0.1 \ L\)
Lower: \(\lambda = 0.5 \ L\)
Monodisperse Disks: Asymptotic Behavior:

- For both isotropic and perfectly aligned monodisperse disks: in the limit that: \( R \to \infty \): Plateau value for the threshold depends linearly upon \((L / \lambda)\)


Solid – Isotropic  
Dashed – Fully aligned, nematic

Monodisperse disks, thresholds calculated in the limit: \( R \to \infty \)

Predicted limiting behaviors:

\[
\phi_c \approx \frac{1}{(5\pi+4)} \left( \frac{L}{\lambda} \right), \text{ Isotropic}
\]

\[
\phi_c \approx \frac{1}{14} \left( \frac{L}{\lambda} \right), \text{ Aligned}
\]
Circular Disks in 3D: Bidisperse Case


- For a fixed value of $(\lambda / L)$: Polydispersity lowers the threshold, for both isotropic and nematic disk arrangements

- Bidisperse system: $\lambda / L = 0.1$ in all cases, and we assume that $R >> L$, $\lambda$

Threshold normalized by its value for a monodisperse system with equal value of $(\lambda / L)$: Isotropic disk orientations

Solid Lines: Lattice model  
Dotted Lines: Integral equation theory  

Upper: $R_2 = 5 \ R_1$, and: Lower: $R_2 = 10 \ R_1$

Horizontal axis, $f_2 = \text{Number fraction of disks with radius equal to } R_2$
Non-random Spatial Distribution of Particles: Heterogeneity effects: Another approach:

- Alternative approach, one that complements the lattice-based model

- VERY SIMPLE, ALTERNATIVE microstructural descriptors that capture mesoscale heterogeneity:

  (i) Pore radius distribution, and moments thereof, e.g. mean pore radius, and:

Pore Radius & Chord Length Distributions (I):

Mean values for the pore radius ($<r>$) and chord length ($l_c$) provide simple and physically transparent means for quantifying spatial non-randomness.

Goal: to construct as simple a description as possible in terms of such variables, and to use these as vehicles to examine the impact of spatial heterogeneity upon elastic moduli.
Pore Radius & Chord Length Distributions (II):

Starting point: Random distribution of rods: we start with a generalization of the traditional Ogston result for the distribution of pore sizes in a fiber network, generalized to partially account for fiber impenetrability:


Pore radius distribution in network of fibers of radius = $R$, volume fraction = $\phi$

$$f(r,\phi) = \left(\frac{2}{R}\right)\ln\left(\frac{1}{1-\phi}\right)\left(1+\frac{r}{R}\right)(1-\phi)^{1+r/R^2}$$

Mean and mean-squared pore radii:

$$\langle r \rangle = \int_0^\infty dr f(r,\phi)r = \left(\frac{R}{2}\right)\sqrt{\frac{\pi}{\alpha}} e^{\alpha} \{1-\text{Erf} \left(\sqrt{\alpha}\right)\}$$

$$\langle r^2 \rangle = \int_0^\infty dr f(r,\phi)r^2 = \left(\frac{R^2}{\alpha}\right)[1-e^{\alpha}\sqrt{\pi\alpha}\{1-\text{Erf} \left(\sqrt{\alpha}\right)\}]$$

where: $\alpha = \ln\left(1/(1-\phi)\right)$
Comparison to Ogston model:

In the traditional Ogston model:

\[ f(r, \phi_0) = \frac{2\phi_0}{R} \left( 1 + \frac{r}{R} \right) e^{-\phi_0 \left( \frac{r}{R} \left( \frac{r}{R} + 2 \right) \right)} \]

where \( \phi_0 \) represents the nominal fiber volume fraction.

Relation between models:

\( \phi_0 \leftrightarrow -\ln(1 - \phi) \)


For small enough rod volume fractions:

\[ \frac{\langle r \rangle}{R} \approx \frac{1}{2} \sqrt{\frac{\pi}{\phi}} \]

and our treatment reduces to that of Ogston when \( \phi \ll 1 \)
Averaging over Fluctuations in $\phi$:

- Simplest possible *ansatz*: bimodal distribution over mesoscale fibre volume fractions, represent distribution over $\phi$ by:

$$
\psi(\phi) = \frac{[(\phi_2 - \langle \phi \rangle)\delta(\phi - \phi_1) + (\langle \phi \rangle - \phi_1)\delta(\phi - \phi_2)]}{(\phi_2 - \phi_1)}
$$

where $\langle \phi \rangle$ = macroscopic fiber volume fraction

This distribution function $\psi(\phi)$ must be interpreted in a strictly operational sense !!!

- Distribution over pore radii, averaged over mesoscopic fluctuations in $\phi$:

$$
F(r) = \frac{1}{(1 - \langle \phi \rangle)} \int_{0}^{1} d\phi \psi(\phi)(1 - \phi)f(r;\phi)
$$

where $f(r;\phi)$ is the result for a random distribution of fibers

- Mean and mean-squared pore radii, and mean chord lengths, can then be expressed in terms of $\{\langle \phi \rangle, \phi_1, \phi_2\}$
Simple estimation of moduli as functions of fluctuations in $\phi$:

- Use the foregoing formalism in *inverse* manner to determine $\{\phi_1, \phi_2\}$ for specified values of $<\phi>$, and for the mean pore radius and chord length.

- Values of $\{<\phi>, \phi_1, \phi_2\}$ then used with Hill average (arithmetic mean) of the Reuss-Voigt bounds (R. Hill, *Proc. Phys. Soc. A* 65, 349, (1952); J. Dvorkin, *et al.*, *Geophysics* 72, 1, (2007)) to estimate modulus in terms of $<r>$ and $<l_c>$.

Solid Line: Modulus for uniform fiber distribution (supplied as *ansatz*).

Upper and lower broken lines: Hill average of Reuss-Voigt bounds, obtained from model when $<r>$ and $<l_c>$ each exceed their values for a random fiber distribution by factors of 2 and 3, respectively.

Basic Conclusion:

- Mesoscale fluctuations in $\phi$ lead to:
  
  (i) increase in the mean pore radius and chord length
  (ii) reduction in the moduli of the material (within the empirical Reuss-Voigt-Hill averaging scheme)

- Alteration in the mean pore radius/pore radius distribution may be expected to also affect transport properties, e.g., the diffusion coefficient for a spherical tracer

- Hindered diffusion model: Cylindrical fibers (radius $R$) pose steric obstacles to motion of a spherical tracer (radius $R_0$), specific interactions neglected
Tracer Diffusion in non-random fiber networks (I)


- Operational volume fraction distribution function $\psi(\phi)$ maps onto distribution over radii in the cylindrical cell model
Tracer Diffusion in non-random fiber networks (II)

For cylindrical cell model: diffusion constant, $D$, for a spherical tracer of radius $R_0$ in system of fibers of radius $R$ satisfies: (L. Johansson, et al., Macromolecules, 24, 6024, (1991)):

$$
\frac{D}{D_0} = \int_{R_0 + R}^{\infty} da \eta(a) \left[ \frac{a^2}{a^2 + (R_0 + R)^2} \right]
$$

where $\eta(a) =$ Distribution over outer radii in cell model, and $D_0 =$ unhindered diffusion constant for the same tracer when fiber volume fraction vanishes.

Mapping procedure using bimodal distribution for $\psi(\phi)$ permits expressing $\eta(a)$ in terms of \{mean pore radius + mean chord length\} for the fiber network as a whole.
Qualitative findings:

- Results of accounting in this manner for spatial fluctuations in $\phi$:
  - For randomly distributed fibers: our approach leads to a value for $D$ that is consistently below $D_{Ogston}$, where $D_{Ogston}$ arises from combining {Ogston result for pore radius distribution + the cylindrical cell model}
  
- Quite generally: Spatial fluctuations in $\phi$ are predicted to increase $D$, so long as diffusion is controlled primarily by steric/excluded-volume effects

Figure shows $D / D_{Ogston}$ for different ratios of the tracer radius ($R_0$) to fiber radius ($R$) for randomly distributed fibers

$$\frac{D_{Ogston}}{D_0} = e^{-\gamma} + \gamma^2 e^{\gamma} E_1(2\gamma)$$

$$\gamma = \langle \phi \rangle (R_0 + R)^2 / R^2$$

$E_1 = \text{Exponential Integral}$
Tracer Diffusion: Some results (I):

- Diffusion of Bovine Serum Albumin (BSA) ($R_0 = 3.6$ nm) in polyacrylamide gel ($R = 0.65$ nm)

1: Fiber distribution random, steric effects only
3: Steric and hydrodynamic factors both included, but fiber distribution *non-random*:

Mean pore radius and chord length are each 1.5 times larger than for a random fiber network with equal $\langle \phi \rangle$

Tracer Diffusion: Some results (II):

- Diffusion of Bovine Serum Albumin (BSA) \( R_0 = 3.6 \) nm in calcium alginate gels \( R = 0.36 \) nm

1: Fiber distribution random, steric effects only
3: Steric and hydrodynamic factors both included, but fiber distribution *non-random*:
   Mean pore radius and chord length are each 1.5 times larger than for a random fiber network with equal \( <\phi> \)
Pore Size Distribution:

- Model for pore size distribution in isotropic, random, fiber networks

- Map fibers with finite, non-zero, hard core radii $R$ onto system of fully penetrable fibers with radii $R_1$ that are allowed to overlap

- Map fiber radii in order to enforce equal surface area per volume for equal values of the volume fractions occupied by the fiber cores (A.P. Chatterjee, *J. Phys.: Condensed Matter*, 24, 375106, (2012))

Leads to:

\[
\begin{align*}
\text{Pore Size Distribution:} \\
&= f_1(r, \phi) = \left( \frac{2}{R_1} \right) \left( \ln \left( \frac{1}{1-\phi} \right) \right) \left( 1 + \frac{r}{R_1} \right) (1 - \phi)^{(1+r/R_1)^2} \\
\text{Mean Pore Radius:} \\
\langle r \rangle &= \int_0^\infty dr f(r, \phi) r = \left( \frac{R}{2} \right) \left( \frac{\sqrt{\pi \alpha}}{\phi} \right) \{1 - \text{Erf}(\sqrt{\alpha})\} \\
\end{align*}
\]

where:

\[
R_1/R = ((1 - \phi)/\phi) \ln(1/(1 - \phi)) \\
\alpha \equiv \ln(1/(1 - \phi))
\]
Mean Pore Radius in Random, Isotropic, Fiber Networks:


- **Lower Curve:** Present work based upon mapping between penetrable and impenetrable rods that preserves surface area per unit volume of network (A.P. Chatterjee, *J. Phys.: Condensed Matter*, **24**, 375106, (2012))
Future Directions

- Modeling frequency-dependent moduli, perhaps by way of the viscoelastic “correspondence principle”

- Generalizations to other particle morphologies, such as persistent/semiflexible linear particles/macromolecules or aggregates such as micelles

- Unification of Bethe-lattice based percolation analyses with simple descriptions of non-random microstructures, connection between lattice model and pore size distribution/mean pore radius
Acknowledgements

From SUNY-ESF:
Dr. Xiaoling Wang
Ms. Darya Prokhorova
Dr. DeAnn Barnhart
Profs. W.T. Winter and I. Cabasso

From other institutions:
Prof. Alain Dufresne
Prof. Henri Chanzy
Prof. Laurent Chazeau
Prof. Christoph Weder
Prof. Jeffrey Capadona
Prof. George Weng
Prof. Paul van der Schoot
Prof. Claudio Grimaldi
Prof. Isaac Balberg
Dr. Ronald Otten
Dr. Biagio Nigro

USDA CSREES National Research Initiative Competitive Grants Program
USDA CSREES McIntire-Stennis Program
National Science Foundation
Research Foundation of the State University of New York